THE EFFECTS OF CATALYSTS ON SHORT CONTACT TIME COAL LIQUEFACTION*

M. G. Thomas, T. C. Bickel, B. Granoff

Process Research Division 4731, Sandia National Laboratories
Albuquerque, New Mexico 87185

Introduction

An understanding of the effects of inherent (1-3) (i.e., naturally occurring mineral matter) and externally added catalysts (4) is of prime importance for the production of synthetic liquid fuels by the direct liquefaction of coal. Future liquefaction process concepts will require an extensive research data base, including the rates and mechanisms of the various chemical steps that occur when solid coals are converted into useful liquid products. (5) In a generic direct coal liquefaction process (Figure 1), the coal/solvent slurry and hydrogen are first preheated to liquefaction temperatures (400-475°C), and are then fed to a catalytic reactor or dissolver. The average residence time in the reactor is generally an order of magnitude greater than that in the preheater. (6) The reactions that occur in the preheat stage involve the dissolution of coal; i.e., the conversion of coal to species (such as preasphaltenes) that are soluble in tetrahydrofuran (THF). (7) All current direct liquefaction processes utilize preheaters where coal dissolution takes place, and they also take advantage of the catalytic effects of the inherent mineral matter in coal.

Short-contact-time (SCT) liquefaction (8), as we define it, refers to the minimum time at a given temperature required for the complete dissolution of the coal. This time is sufficiently long to convert the coal to preasphaltenes, but is short enough so that secondary reactions (i.e., the conversion of preasphaltenes to toluene and pentane solubles) take place to only a limited extent. Traditionally, the initial dissolution step has not been considered in catalyst studies, generally due to the belief that this step cannot be catalytically enhanced. We will show that catalysts do have an effect on SCT liquefaction. First, however, we will describe a mechanistic pathway for coal liquefaction reactions. Following this, we will discuss the role of catalysts and the potential impacts of catalysis on current and future liquefaction processes.

Discussion

The following series reaction path for coal liquefaction is in agreement with the bulk of literature data: (9-10)

      1. coal + solvent ⇌ preasphaltene

      2. preasphaltene ⇌ asphaltene

      3. asphaltene → oil

The first step of this reaction is usually considered to be non-catalytic; i.e., solid coal plus solid catalyst plus a source of hydrogen is a very unlikely type of reaction. In addition, molecular hydrogen does not appear to have a significant involvement in the dissolution process.

The secondary reactions, 2 and 3, are considered to be solution phase reactions and do involve hydrogen transfer. Direct interaction between hydrogen gas and model compounds has been observed, but the more usual mechanism is the transfer of hydrogen through the solvent. (11-12) This reaction in particular appears to be catalytically enhanced.

At this point, one needs to reassess the possibility of catalyst affecting the dissolution step. There are marked solvent quality effects both in upgrading and in coal dissolution.(13-14) Because the interconversions of the preasphaltenes, asphaltenes and oil are affected by catalysts, and because these moieties are parts of the solvent which affects dissolution, it follows that catalysts are affecting coal dissolution. The existence of the solvent quality effect also unequivocably establishes that solvent is an integral reactant (not just a medium) in the first step of dissolution.

In Figure 2, two examples of catalytic effects of mineral matter on liquefaction are shown. (15) These examples are specific to FeS_2, since FeS_2 has been shown to be the most active catalytic species in mineral matter. In Figure 2a, we have shown enhanced conversion with the incremental addition of FeS_2. This indicates apparent rate enhancement although insufficient data were collected to compare rate constants. At constant conversion, Figure 2b, a selectivity to oil (as opposed to gas make) is obtained by the addition of 5 wt % pyrite and lowering the reaction temperature by 25°C.

An example specific to SCT liquefaction is shown in Figure 3. (16) Here we have shown the marked effect of the addition of FeS_2 on the dissolution and conversion of coal at temperatures where secondary reactions are not observed. An $\sim$ 15 wt % increase in THF solubles and a complete regime change from solvent imbalance (negative toluene solubles) to a small positive conversion to toluene solubles is observed.

These examples have demonstrated marked effects, both in apparent rate enhancement and in product selectivity. However, to optimize the possible catalyst effects, we need to properly utilize: (1) the Fe-S system; and (2) the reactivity of the coal-derived products.

The Fe-S system has been studied in detail both in the presence and absence of H_2. In 1947, Schwab and Phillinis (17) measured the decomposition of FeS_2 in a TGA apparatus and determined rates and activation energies. Although the rates were affected by the presence of hydrogen, the activation energy was measured to be $\sim$ 30 kcal/mole in each case. The measurements point out that hydrogen is not part of the activated complex of the rate determining step; i.e., hydrogen adsorption and dissociation may occur but does not affect the rate of decomposition of pyrite. A mechanism consistent with the data is:

$$FeS_2 \rightleftharpoons FeS + S$$
$$S + H_2 \rightleftharpoons HS + H$$
$$H + HS \rightleftharpoons H_2S$$
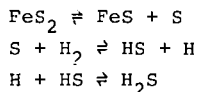
Paramount in this description is the concept that this in an equilibrium system and that no individual species involved can be described separately to explain the observed catalytic effects. In an operational sense, it is most likely the H_2S fugacity which controls the equilibrium and establishes our steady state activity.

The rate of decomposition is affected by coal and solvent, but the activation energy is not a function of the system (i.e., external atmosphere). Rate constants for the decomposition, at 350°C, in the presence of coal and solvent, solvent and hydrogen, and with hydrogen alone have been calculated, $k_{coal+solvent} = 4 \times 10^{-2}$ mole/min, $k_{solvent} = 4.5 \times 10^{-2}$ mole/min, $k_{H_2} = 1.9 \times 10^{-1}$ mole/min. (18)

Our second approach to catalyst activity regards the response of the substrate molecules (e.g., preasphaltenes) to "catalytic" treatment. A method developed for obtaining and observing effects is shown in Figure 4. (6) Three preasphaltenes, differing in reactivity, were prepared in three separate autoclave runs at 350°C/30 minutes, 405°C/5 minutes, and 430°C/30 minutes, all at ~ 1800 psig H_2. Preasphaltenes were isolated by solvent extraction techniques, and their subsequent reactivities were measured in microreactor experiments at 400°C, 10 minutes, and 450 psig H_2. The thermal reactivity (no added catalyst) is shown in Figure 4a as a cross-hatched plane, where the conversion of the preasphaltenes was plotted against the time and temperature at which they were prepared. The speckled plane was obtained by analogous experiments with the addition of a ground supported CoMo catalyst-- American Cyanamid 1442A CoMo.

The slope of the plane for the catalyzed runs is greater than that observed for the thermal runs, which indicates a rate enhancement by CoMo. More importantly, the two-plane surfaces intersect. This intersection is a line by definition, Figure 4b. (Increasing the number of points would probably produce non-plane surfaces intersecting in a curve.) This line of intersection describes the demarcation of substrate reactivity between observable catalytic effects, and non-observable catalytic effects. This analysis is catalyst-specific, and our description is reaction-specific for the decomposition of preasphaltenes. Thus we have a way to: (1) test for catalytic activity; and (2) determine when and where catalyst should be employed.

Summary

The effects of catalyst on the early stages of coal liquefaction have been described in terms of changes in dissolution and product distribution. The major points established for SCT liquefaction include:

1. Catalysts of some form are present during the initial stages of all direct liquefaction processes;

2. Catalysts affect both dissolution (indirectly) and secondary reactions; and

3. Coal-derived materials that have been formed at short times are more thermally reactive and more sensitive to subsequent catalytic treatment than coal-derived materials that have been formed at longer residence times.

References

1. P. A. Montano, B. Granoff, Fuel, 59, 214 (1980).

2. J. A. Guin, J. M. Lee, C. W. Fan, C. W. Curtis, J. L. Lloyd, A. R. Tarrer, Ind. Eng. Chem. Process Des. Dev., 19, 440-446 (1980).

3. B. Granoff, P. M. Baca, M. G. Thomas, G. T. Noles, "Chemical Studies on the Synthoil Process: Mineral Matter Effects, Final Report," Sandia National Laboratories Report SAND-78-1113 (1978).

4. A. G. Comolli, R. R. Bernard, E. S. Johanson,, Proc. 14th Intersociety Energy Conv. Eng. Conf., $\underline{1}$, 815-820 (1979).

5. E. C. Moroni, "DOE Overview – Advanced Direct Coal Liquefaction," Fifth Annual Contractor's Conference, EPRI, Palo Alto, CA, May 7-8 (1980).

6. T. C. Bickel, R. M. Curlee, B. Granoff, T. D. Padrick, F. V. Stohl, M. G. Thomas, "Coal Liquefaction Process Research," Sandia National Laboratories Report SAND-80-1426 (1980).

7. R. C. Neaval, Fuel, 55, 237 (1976).

8. DOE Conference on Advanced Two-Stage Liquefaction, Albuquerque, NM February 26-27 (1980).

9. M. G. Thomas, R. K. Traeger, Prep. American Chemical Society, Division of Fuel Chemistry, $\underline{24}$ (3) 224 (1979).

10. Y. T. Shah, D. C. Cronauer, A. G. Mclluried, J. A. Pasaskos, Ind. Eng. Chem. Process Des. Dev., 17 (3) 288 (1978).

11. D. D. Whitehurst, T. O. Mitchell, Prep. American Chemical Society, Division of Fuel Chemistry, 21, 5, 127 (1976).

12. M. G. Thomas, T. C. Bickel, Prep. American Chemical Society, Division of Fuel Chemistry, 27, 38 (1980).

13. D. G. Cronauer, D. M. Jewell, Y. T. Shah, R. J. Modi, Ind. Eng. Chem. Fundam., 18 (2) 152 (1979).

14. J. A. Kleinpeter, F. P. Burke, P. J. Dudt, D. C. Jones, "Process Development for Improved SRC Options: Interim Short Residence Time Studies," EPRI Report AF-1158, Conoco Coal Development Company (1979).

15. B. Granoff, P. A. Montano, "Mineral Matter Effects in Coal Liquefaction," Conf. on the Chem. and Phys. of Coal Util., W. Va. Univ., June 2-4 (1980); also Ref. 3.

16. Unpublished results, Sandia National Laboratories.

17. George-Marin Schwab, J. Philinis, JACS, 69, 2588 (1947).

18. M. G. Thomas, T. D. Padrick, F. V. Stohl, "The Decomposition of Pyrite Under Coal Liquefaction Conditions: A Kinetic Study," submitted for pub. in Fuel, October (1980).
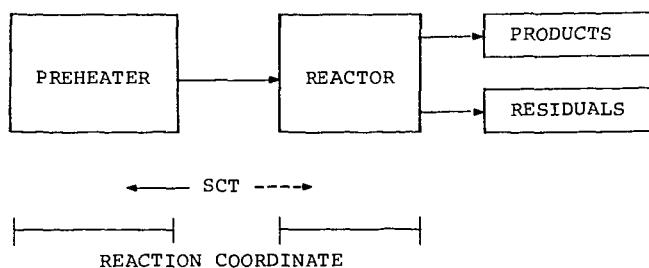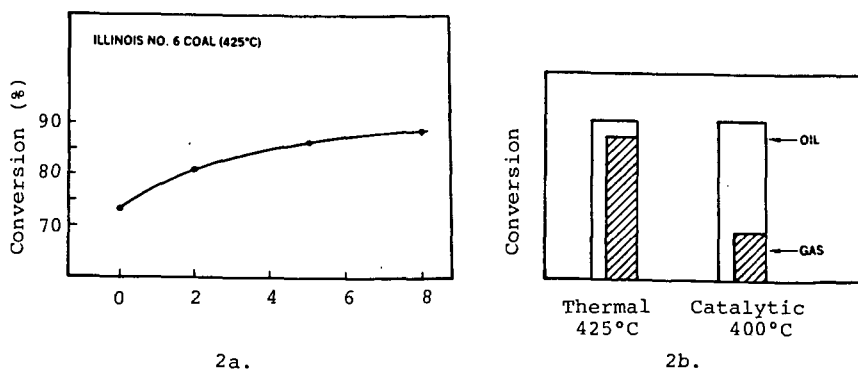
Figure 1. A Generic Description for Coal Liquefaction

2a.
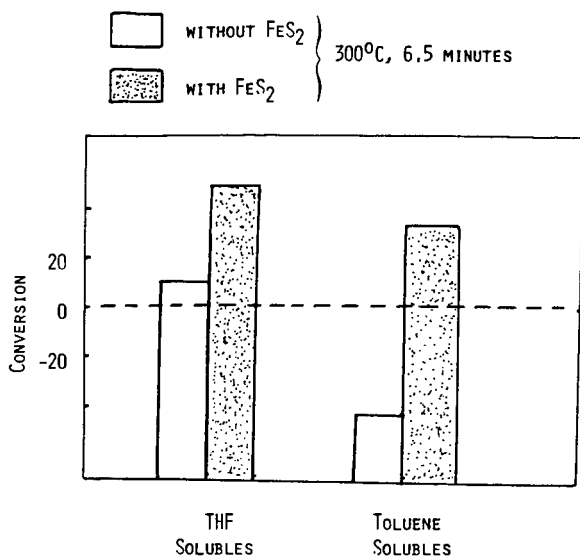

2b.

Figure 2. Effect of Mineral Matter on Liquefaction

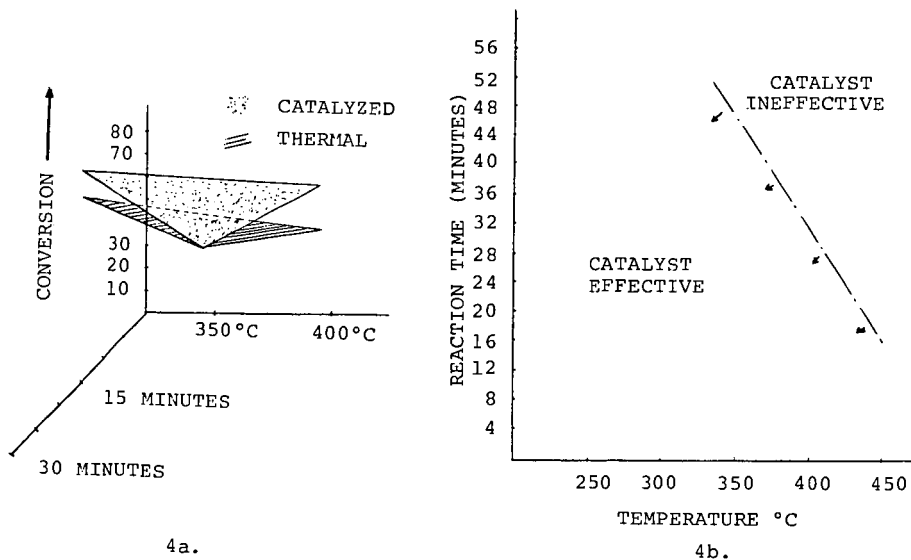Figure 3. Catalysis of Dissolution by FeS$_2$

4a.

4b.

Figure 4. The Effect of Preasphaltene Reactivity on
Obtaining and Observing Catalytic Responses